Biogas upgrade via ex-situ technologies

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Abstract The biological upgrade of biogas to biomethane (CH_4 > 90%) is a popular emerging technology, since the produced CO_2 is not removed but is converted to biomethane using hydrogen (H_2). The initial aim of the present study is the acclimatization of a microbial population derived from a typical biogas plant, under high concentrations of H_2, as well as the development of an enriched biomass in hydrogenotrophic methanogens. The enriched biomass was used to inoculate ex-situ bioreactors for biomethane production under continuous operation. Specifically, a bubble reactor and a trickle bed reactor were studied, and their performance was compared under the same operating conditions. Both reactors were provided with a mixture of H_2, CH_4 and CO_2, which was injected through a conventional diffuser. The methane content in the upgraded biogas reached 92.7±1.1% and 95.7±1.1% for bubble and trickle bed reactor respectively, under a loading rate of 1.26 L_{H2} $L_{reactor}^{-1}$ d^{-1} (11.5h gas retention time). However, at increased H_2 loading rates the trickling bed reactor outperformed the bubble reactor.

Keywords: biogas upgrade, anaerobic digestion, biomethane, hydrogenotrophic methanogenesis

1. Introduction

Biogas is the main product of anaerobic biodegradation of organic wastes. This process, known as anaerobic digestion, takes place through a combination of metabolic pathways performed via the synergistic function of bacteria and archaea (Bassani et al., 2015). Biogas consists mainly of 50-70% CH_4 and 30-50% CO_2. Traces of other gases are also found in biogas, which are either metabolic products such as hydrogen sulfide (H_2S) and ammonia (NH_3) or come from the treated waste such as siloxanes (Angelidaki et al., 2018). The produced biogas, due to the high energy content of CH_4 (36 MJ / m^3 under normal conditions), is usually used in cogeneration machines (CHP).

Issues arising from the increased greenhouse gas emissions, such as CO_2, require the development of technologies to drastically reduce them (Mikkelsen et al., 2010). The biological conversion of CO_2 into useful products, such as CH_4, is a promising alternative that takes place under mild conditions of temperature and pressure without the need of using chemicals (Alitalo et al., 2015; Bassani et al., 2017). Combining the process of CO_2 biological reduction via hydrogenotrophic methanogenesis, the calorific value of biogas can be increased, since the CO_2 is converted to CH_4. The final product is called biomethane and it resembles natural gas in chemical composition (Bassani et al., 2016). The main advantage of biomethane over natural gas is that the former is a renewable energy source, since the raw material used for its production is organic waste (agro-industrial wastes, municipal sludge, animal wastes, etc.).

During the biological upgrade of biogas H_2 is provided from an external source, which in conjunction with the CO_2 are consumed by the hydrogenotrophic archaea to produce CH_4. The required H_2 should be produced via water electrolysis using only the excess renewable electricity (such as solar or wind energy) which exceeds the capacity of the grid. In this way, the total carbon contained in the treated organic wastes is utilized, resulting in an increased energy production. Furthermore, the storage of surplus renewable energy is achieved, since the upgraded biogas can now be injected into the gas grid (Alitalo et al., 2015). Utilizing the current natural gas facilities, biomethane can be transferred from its production area, mainly rural areas with low energy consumption, to urban centers with increased energy requirements (Agneessens et al., 2018).

Several studies have demonstrated that biomethane production is efficient, achieving a CH_4 content in the final gas mixture over 95% (Bassani et al., 2017; Porte et al., 2019). However, it is clear that there are several technical challenges that need to be addressed in order to develop a sustainable and resilient technology. The most important issue is the low solubility of hydrogen in the liquid phase, which restricts its contact with methanogens. Another issue is the consumption of CO_2, which leads to an increased pH (>8) of the mixed liquor, resulting into methanogenesis inhibition (Kougias et al., 2017). The aim of the present study is the development of an enriched biomass in hydrogenotrophic methanogens, in order to inoculate different types of ex-situ bioreactors for continuous biomethane production. The efficiency of the studied bioreactors was evaluated taking into account the substrates conversion and other factors such as the pH and the VFAs accumulation, which are essential to evaluate the systems resilience.

2. Materials and methods

2.1. Biomass acclimation

The inoculum came from a full-scale anaerobic digester treating agro-industrial wastes, operating at the mesophilic temperature range (Spyridonidis et al., 2020). Prior to the inoculation, a 2mm sieve was used to remove the large particles, from the biomass. The inoculum was also diluted, at a ratio of 1:1, with nutrient medium prepared according to Bassani al., 2016. A column with a working volume of 2L and a gas phase of 0.92L was used for the biomass acclimatization process. A gas tight aluminum bag was used to store a gas mixture of H_2, CH_4, and CO_2 at a ratio of 59.7: 24.2:16.2. The gas mixture was recirculated through the bioreactor, at a rate of 4L $L_{reactor}^{-1}$ h^{-1}, via a conventional diffuser placed at the bottom of the column, using a peristaltic pump. As soon as the H_2 of the gas mixture was converted to CH_4, the feeding procedure was repeated with a fresh gas mixture till the concentration of VSS in the liquid reached the value of 500mg L^{-1}. Thereafter, a dilution with the nutrient medium at a ratio of 1:1 took place. The procedure of successive feedings and dilution was repeated several times in order to develop a microbial consortium composed mainly by hydrogenotrophic methanogens. The temperature was maintained at the mesophilic range (38.5 – 39°C).

2.2. Continuous biomethane production

A bubble reactor and a trickle bed reactor were used to produce biomethane in continuous operation, which were inoculated with the acclimatized biomass developed at the previous stage. The working volumes of the bubble reactor and the trickle bed reactor were 2L and 1.25L respectively, while the gas phase was approximately the same (0.9L) for both bioreactors. Both reactors were continuously fed with a gas mixture of H_2, CH_4, and CO_2 at a ratio of 59.7: 24.2: 16.1, which was introduced via diffusers, using peristaltic pumps. To increase the contact between the gaseous substrates and the biomass in the bubble reactor, gas recirculation took place at a rate of 4L $L_{reactor}^{-1}$ h^{-1}, using a peristaltic pump. The trickling bed reactor was filled with polyethylene rings (Kaldnes K1) as packing material (specific surface area 800 m^2 m^{3-1}). During the start-up, the reactor was filled with the synthetic medium containing the inoculum at a concentration of 330ml L^{-1}, and the liquid was recirculated and equally trickled over the bed. Both bioreactors, as well as the glass vessel, were operating at mesophilic temperature (39±1°C).

3. Results and discussion

3.1. Results of acclimation process

At the beginning of the experiment till day 19, the conversion of H_2 was high (97.9 ± 2.09%), and the CH_4 content in the final gas mixture was 92.85 ± 2.7% (Figure 1). However, acetic acid was accumulated at concentrations greater than 500mg L^{-1} (data not shown here). To avoid the accumulation of acetic acid favored at high H_2 concentration by the homoacetogens (Agneessens et al., 2018), the gas mixture in feeding was diluted with nitrogen at a ratio N_2: H_2: CO_2: CH_4 - 50.0: 29.8: 8.0: 12.2. The dilution resulted in a higher CH_4 content in the final gas mixture (95.66 ± 1.35%) excluding N_2 from the calculation of the biogas composition (Figure 1), while the acetic acid concentration was zeroed. On day 123 accumulation of acetic acid took place reaching a concentration of 150 mg L^{-1} approximately, which remained constant till the end of the experiment. This indicates that the conversion of H_2 to CH_4 probably does not take place only through hydrogenotrophic methanogenesis, but also via acetotrophic methanogenesis using the acetate produced by homoacetogens.

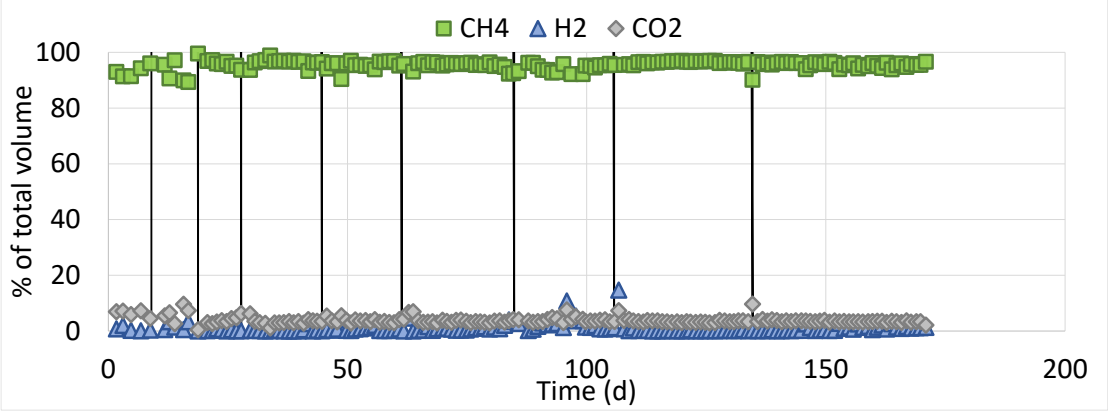

Figure 1: Gas mixture content of CH_4, H_2, CO_2 during the biomass acclimation process. The vertical lines indicate when the dilution of the reactors liquid with nutrient media took place.

3.2. Performance of biogas upgrade reactors

The efficiency for both bubble and trickle bed reactors was studied at three different gas retention times (GRT). At Period I, in which the GRT was set at 15.4h, the efficiency was similar for both reactors and the CH_4 content in the effluent gas mixture was exceeding 96% (Table 1). Increasing the H_2 loading rate at Period II, resulted into a slight decrease of the bubble reactor efficiency, while the performance of the trickling filter remained constant. Even though the efficiency of trickling filter did not decline, acetic acid was accumulated in concentrations greater than 300 mg L^{-1} (Table 1). A further reduction of the GRT at 7 hours (Period III) resulted in a significant decrease in the efficiency of the bubble reactor leading into a CH_4 content in the effluent gas mixture of 64.4±6.0%. The reduced yield is due to the drop in pH (6.28±0.13), which was the outcome of the acetic acid accumulation at concentrations higher than 900 mg L^{-1}. At such pH values, the function of both metabolic pathways of methanogenesis (acetotrophic and hydrogenotrophic) are significantly inhibited. On the contrary, the efficiency of the trickling filter during the Period III, remained stable and the CH_4 content was above 97% in the effluent gas mixture. The acetic acid concentration was slightly increased (425±3 mg L^{-1}) without leading to a significant pH drop and affecting the performance of the process.

Table 1: Reactors performance for each experimental period

Period	I	II	III
GRT (h)	15.39	11.48	7.19
H_2 Loading rate (L $L_{reactor}^{-1}$ d^{-1})	0.94	1.26	1.99
Bubble reactor			
CH_4 (%)	96.0±1.8	92.7±1.1	64.4±6.0
H_2 Conversion (%)	99.1±0.1	97.8±1.7	87.0±3.3
Acetate (mg L^{-1})	28±19	47±7	918±161
pH	7.81±0.17	7.46±0.13	6.28±0.13
Trickling filter reactor			
CH_4 (%)	97.6±1.1	95.7±1.1	97.2±0.4
H_2 Conversion (%)	99.8±0.1	99.7±0.2	99.8±0.1
Acetate (mg L^{-1})	44±9	307±114	425±3
pH	7.77±0.16	7.47±0.15	7.48±0.01

Both reactors were operated under mesophilic conditions. At the research of Luo and Angelidaki 2012, the process of biological biogas upgrade was experimentally proven to be more efficient under thermophilic conditions in comparison to the mesophilic range. However, the efficiency of the trickling filter at the present work is similar to the study of Hugo Porte et al., 2019 who tested two trickling filters under the same operating conditions at thermophilic temperature (54±1°C).

4. Conclusions

At the present study, the biological biogas upgrade is demonstrated to be efficient (CH_4 content was above 96%) for both bubble reactor and trickling filter reactor, under mesophilic conditions. However, when GRT has reduced to 7h, the trickling filter outperformed the bubble reactor, since the increased H_2 loading rate in the bubble reactor resulted in a high acetate accumulation and therefore in a severe pH drop. On the other hand, the performance of the trickling filter remained stable under all studied GRTs (H_2 conversion was above 99%) proving to be a robust technology for biological biogas upgrade.

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